

EVIDENCE RELEVANT TO THE LIFE ON MARS DEBATE. (2) AMINO ACID RESULTS.

I.P.Wright¹, M.M.Grady^{1,2} and C.T.Pillinger¹. ¹Planetary Sciences Research Institute, Open University, Walton Hall, Milton Keynes MK7 6AA, UK (i.p.wright@open.ac.uk); ²Natural History Museum, Cromwell Road, London SW7 5BD, UK (m.grady@nhm.ac.uk).

Following on from a companion abstract [1], it has been suggested by McDonald and Bada [2] that EETA 79001 (hereafter E79) has been contaminated by terrestrial amino acids. The basic observation is that E79 contains 1-0.4 ppm of amino acids that are almost exclusively L-enantiomers - since the amino acids concerned are commonly found in proteins, the conclusion is that they are thus terrestrial contaminants. The mechanism of introduction of the amino acids into E79, during its 12,000 year sojourn in Antarctica, is assumed to be by inundating meltwater carrying organic compounds. Amino acids were considered to have been selectively retained by the carbonate minerals - McDonald and Bada [2] cited Carter [3] and Carter and Mitterer [3] as supporting evidence for this putative phenomenon. We now consider the implications of this.

Firstly, since ice from the Allan Hills area of Antarctica contains 1 ppb of amino acids [2] it is apparent that in order to get 1-0.4 ppm of said compounds into E79 it is necessary to flush between 400 and 1000 times the rock mass of meltwater through the sample (i.e. $3-8 \times 10^6$ g of water). The ramifications of such an event would be considerable - indeed, it would be surprising if any of the rock survived. Since Antarctic ice has a relatively low $\delta^{18}\text{O}$ (typically -40 to -55‰ [5]) compared to that of the meteorite itself (+4.2 to +4.3‰ [6,7]) the effects of extensive water-rock interaction would be, at very least, to have re-set the oxygen isotopic composition of the carbonates to isotopically light values. Since the $\delta^{18}\text{O}$ values of the carbonates in E79 [8,9] are about the same as those in other non-Antarctic martian meteorites [10] it is clear that no such isotopic equilibration has taken place.

Secondly, the putative trapping mechanism [2] is open to criticism; it is claimed that it is the carbonates in E79 that selectively remove amino acids from the meltwater. This is incompatible with the observation that the druse sub-sample [2] contains 1 ppm amino acids whereas an ostensibly druse-free sample of the lithology A part of the meteorite contains 0.4 ppm [2]. Consider that the druse sample analysed by Wright et al. [11] contained 2500-3500 ppm C as carbonate; it is considered that the minimum concentration of carbonate below which a sample cannot be recognised as containing druse is equivalent to 200 ppm C as carbonate. Thus, a reasonable range of carbonate

concentrations for the druse samples of E79 is 200-3500 ppm C (although note that the upper limit could theoretically be 120,000 ppm C, i.e. pure carbonate). Estimates for the carbonate concentration of bulk E79 (i.e. lithology A and B) are probably more compatible with a range of 1-10 ppm C (such a measure, for instance, is obtained from analyses of bulk samples [12], and making some assumptions about end-member isotopic compositions). Note also that an upper limit of 16 ppm C as carbonate was obtained from analyses of band-saw fines from E79 [13]. Furthermore, the carbonate associated with lithology C (the shock-produced glass) contains the equivalent of about 10 ppm C [14]. Thus, the carbonate concentration of bulk E79 is in the range 1-16 ppm, which gives a ratio of carbonate for druse/bulk of 12.5-3000. In other words, if carbonates *are* responsible for "trapping" amino acids, having got 1 ppm in the druse sample it would have been expected that there would be between 0.08 and 0.0003 ppm in the bulk. This is clearly different from the 0.4 ppm which was measured [2]; in fact, the similarity in overall concentrations of amino acids in the druse and bulk samples raises concerns over laboratory-based contamination.

Next we consider the distribution of amino acids in E79 using data from a reference cited by McDonald and Bada [2]. This includes absolute concentrations of three amino acids (glycine, alanine and aspartic acid) determined in grain-size fractions of a sediment sample from the West Flower Garden reef complex from the Texas shelf in the Gulf of Mexico [4]. The sample concerned is predominantly coral debris, being composed mainly of calcium carbonate. While the coarse grain size fraction of the sediment is mostly carbonate (which would have been 12 wt% C if pure), the finer fractions are dominated by a terrigenous, non-carbonate mineral component. The overall concentration of aspartic acid is enriched in the carbonate-rich fraction of the sediment relative to the carbonate-poor, fine material (in a ratio of about 2/1). For E79 [2] the ratio of aspartic acid concentrations in druse versus bulk is 12/1, which is significantly different from the case of the terrestrial sediment, but in the right sense (i.e. a carbonate-rich druse versus carbonate-poor bulk). In contrast, glycine and alanine in the West Flower sediment are enriched in the carbonate-poor part of the sample (in ratios for carbonate-rich to carbonate-poor of about 1/3 and 1/2

LIFE ON MARS. (2) AMINO ACID RESULTS: I.P.Wright et al.

for glycine and alanine respectively). The corresponding ratios for E79 are about 3/1 and 2/1 (glycine and alanine) for druse to bulk, which are both in the wrong sense. It is not possible to comment further on these discrepancies, but it should be pointed out that the sediments [4], which were laid down in a marine environment, in no way approximate the case of E79 containing an overall concentration of 1-16 ppm C as carbonate.

An observation not made in ref. 2 is that the ratio of C in carbonate/organics from the West Flower sedimentary grain-size fractions [4] is typically 40. The results for the druse sample analysed by Wright et al. [11] equate to a carbonate/organics ratio of about 3. In other words, the proportion of organic compounds in carbonate-rich terrestrial sediments is lower than that associated with the druse carbonates in E79. It is this enrichment of organic compounds in E79 that stands out as being unusual. The reasons for this are unclear; an understanding of this observation may be at the root of constraining an important martian process.

That leaves us with the evidence from the D/L ratios of the amino acids [2]. Interpretation of D/L ratios is as follows: a value of 0 (i.e. pure L) represents biogenically produced, or otherwise utilised, compounds, whereas a so-called racemic (i.e. 50:50) mixture with D/L of 1 is considered to result from purely biological processes. But this is an oversimplification. For instance, a slight lowering of the racemic ratio is observed in abiotic processes at the Earth's surface as a consequence of optical activity associated with reflected sunlight. Furthermore, purely abiotic formation processes that produce enriched or depleted D/L ratios are currently being evaluated for commercial exploitation [15]. In contrast, compounds formed by biological activity that are subsequently buried in sediments and subjected to diagenetic processes undergo gradual enrichments in D/L ratios as the enantiomers begin to equilibrate towards racemic mixtures (which can then be added back to the surface pool). Furthermore, it now appears that the abiogenically formed amino acids in carbonaceous chondrites may have D/L ratios not of 1, but of 0.85 ± 0.03 (alanine) or 0.54 (glutamic acid) [16]. This is confirmed by new work that suggests ratios of 0.82-0.66, thought to be the result of formation in an astrophysical environment where the action of circularly polarised light plays an important part [17]. So, the exact significance of the D/L ratios in amino acids from E79 is somewhat ambiguous. Notwithstanding this, if we accept the results at face value the apparent enrichment in the L-enantiomers can be explained in one of two ways; either the amino acids are terrestrial contaminants, or the result of biological

activity on Mars. The latter is a suggestion first made in ref. 2.

Similar conclusions regarding contamination of martian meteorites on Earth, have been made on the strength of arguments involving PAHs [18]. These also look less convincing upon close scrutiny. A more coherent picture will doubtless emerge when comprehensive analyses are made of the several 100 ppm C as organics in E79, rather than the odd ppm of PAHs or amino acids.

References: [1] Wright, I.P. et al. (1997) *Lunar Planet. Sci.*, XXVIII, (this volume); [2] McDonald, G.D. and Bada, J.L. (1995) *Geochim. Cosmochim. Acta*, 59, 1179-1184; [3] Carter, P.W. (1978) *Geochim. Cosmochim. Acta*, 42, 1239-1242; [4] Carter, P.W. and Mitterer, R.M. (1978) *Geochim. Cosmochim. Acta*, 42, 1231-1238; [5] Epstein, S. et al. (1965) *J. Geophys. Res.*, 70, 1809-1814; [6] Clayton, R.N. and Mayeda, T.K. (1996) *Geochim. Cosmochim. Acta*, 60, 1999-2017; [7] Franchi, I.A. et al. (1997) *Lunar Planet. Sci.*, XXVIII, (this volume); [8] Clayton, R.N. and Mayeda, T.K. (1988) *Geochim. Cosmochim. Acta*, 52, 925-927; [9] Wright, I.P. et al. (1988) *Geochim. Cosmochim. Acta*, 52, 917-924; [10] Wright, I.P. et al. (1992) *Geochim. Cosmochim. Acta*, 56, 817-826; [11] Wright, I.P. et al. (1989) *Nature*, 340, 220-222; [12] Wright, I.P. et al. (1986) *Geochim. Cosmochim. Acta*, 50, 983-991; [13] Wright, I.P. et al. (1993) *J. Geophys. Res.*, 98, 3477-3482; [14] Wright, I.P. and Pillinger, C.T. (1994) *Phil. Trans. Roy. Soc. Lond. (A)*, 349, 309-321; [15] Nugent, W.A. (1993) *Science*, 259, 479-483; [16] Engel, M.H. et al. (1990) *Nature*, 348, 47-49; [17] Cronin, J.R. and Pizzarello, S. (1996) *MAPS*, 31, A32; [18] Becker, L. et al. (1997) *Geochim. Cosmochim. Acta*, (in press).